## AFRL-SR-BL-TR-98-REPORT DOCUMENTATION PAGE Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instruction the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget for Information 1. AGENCY USE ONLY (Leave blank) 2. REPORT DATE 3. REPURT TYPE AND DATES COVERED 5 Feb 98 FINAL TECHNICAL RPT, 01 MAR 95 TO 31 AUG 97 4. TITLE AND SUBTITLE 5. FUNDING NUMBERS High Resolution Molecular Spectroscopy of Atmospheric Sciences F49620-95-1-0239 6. AUTHOR(S) Dr. Jyotsna M. Dutta 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER North Carolina Central University 1801 Fayetteville Street Durham NC 27707 9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSORING/MONITORING AFOSR/NM **AGENCY REPORT NUMBER** 110 Duncan Avenue Suite B115 Bolling AFB DC 20332-8050 19980331 0 11. SUPPLEMENTARY NOTES 12a. DISTRIBUTION AVAILABILITY STATEMENT 12b. DISTRIBUTION CODE Approved for public release; distribution unlimited. 13. ABSTRACT (Maximum 200 words) During this project period the temperature dependence of the collision-broadened line widths of few selected lines of SO<sub>2</sub> and H<sub>2</sub>S were studied between 90 K and 600 K. Selected lines were 18(3,15)-18(2,16), 4(2,2)-3(1,3), 13(1,13)-12(0,12), and 26(4,22)-26(3,23) transitions of SO<sub>2</sub> at 204.246 GHz, 235.151 GHz, 251.199 GHz, and 280.807 GHz respectively, and 1(1,0)-1(0,1) and 2(2,0)-2(1,1) transitions of H<sub>2</sub>S at 168.762 GHz and 216.710 GHz respectively. The broadening gases were $N_2$ , $O_2$ , $H_2$ , and He. Reported pressure broadening results of SO<sub>2</sub> and H<sub>2</sub>S extends for the first time to such a wide range of temperature. The newly developed Fast Scan Submillimeter Spectroscopic Technique (FASSST) was applied to investigate HNO<sub>3</sub>. A brief description of the system and some preliminary results related to HNO3 are included in the text below. 14. SUBJECT TERMS 15. NUMBER OF PAGES

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ABSTRACT

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#### COMPLETED PROJECT SUMMARY

RESEARCH TITLE: High Resolution Molecular Spectroscopy of Atmospheric Species

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INCLUSIVE DATES: 01 March 1995 - 31 August 1997

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#### **PUBLICATIONS:**

1.(with) C.D. Ball, T. M. Goyette, P. Helminger, and F. C. DeLucia, "The Pressure Broadening of SO<sub>2</sub> by N<sub>2</sub>, O<sub>2</sub>, He, and H<sub>2</sub> between 90 and 500 K." J. Quant.Spectrosc. Radiat. Transfer **56**, pp. 109-117, 1996.

2.(with) C.D. Ball, M. M. Beaky, T. M. Goyette, and F. C. DeLucia, "Variable Temperature Pressure Broadening of  $H_2$  S by  $O_2$ , and  $N_2$ ." submitted for publication.

#### PRESENTATION OF PAPERS IN NATIONAL AND INTERNATIONAL MEETINGS

1.(with) C. D. Ball, T. M. Goyette, P. Helminger, and F.C.DeLucia, "Variable Temperature Pressure Broadening of H<sub>2</sub>S," International Symposium on Mole. Spectroscopy, Columbus, OH June 10-14, '96.

2.(with) C. D. Ball, T. M. Goyette, and F.C.DeLucia, "Variable Temperature Pressure Broadening of SO<sub>2</sub> and H<sub>2</sub>S," Twentieth Int. Conf. on IR & MM Waves, Orlando, FL December 11-14, 1995

3.(with) T. M. Goyette, C. D. Ball, and F. C. DeLucia, "Variable Temperature Pressure Broadening Of SO2," International Symposium on Molecular Spectroscopy, Columbus, OH, June 12-16, 1995.

#### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project was involved in the millimeter and submillimeter measurement on temperature dependence of pressure broadening of selected lines of molecular species of atmospheric importance. In addition, the newly developed fast scan submillimeter spectroscopic technique (FASSST) was applied to investigate HNO<sub>3</sub> to evaluate its speed and versatility. A brief description of this new spectroscopic system and some preliminary HNO<sub>3</sub> results are given below.

- (1) The pressure broadening of the 18(3,15)- 18(2,16), 4(2,2)-3(1,3), 13(1,13)-12(0,12), and 26(4,22)-26(3,23) transitions of  $SO_2$  at 204.246 GHz, 235.151 GHz, 251.199 GHz, and 280.807 GHz respectively has been studied in the temperature range between 80 K to 600 K. Collision studies were performed both with the atmospherically significant  $N_2$  and  $O_2$  as well as  $H_2$  and  $O_3$  He. (See publication 1 for details)
- (2) The pressure broadening of the 1(1,0)-1(0,1) and 2(2,0)-2(1,1) transitions of  $H_2S$  at 168.762 GHz and 216.710 GHz respectively has been studied over a wide range of temperature which is 90 K to 500 K. The broadening gases were  $N_2$ ,  $O_2$ ,  $H_2$ , and He. (Part of this work has been discussed in detail in publication 2. Rest is discussed more in detail below and a manuscript is under preparation.)
- (3) The newly developed Fast Scan Submillimeter Spectroscopic Technique (FASSST) was applied to investigate HNO<sub>3</sub>. A brief description of the system and some preliminary results are included in the text below.
- (4) Dependences of room temperature pressure broadening parameters and the temperature exponents with the rotational quantum numbers were investigated.
- (5) Reported pressure broadening results of SO<sub>2</sub> and H<sub>2</sub>S extends for the first time to such a wide range of temperature.

#### Accomplishments/New Findings:

#### 1. Variable Temperature Pressure Broadening of SO<sub>2</sub>

Please see publication 1 for detailed discussion on this topic (one copy is enclosed).

#### 2. Variable Temperature Pressure Broadening of H<sub>2</sub>S

Until very recently, the  $H_2S$  molecule was minor atmospheric pollutant introduced to the atmosphere through mainly by natural sources and the processing of oil and coal containing sulfur. However, a new  $H_2S$  source appeared with the introduction of car catalysts which reduce sulfur [1]. These emissions have increased the interest in spectroscopic studies. Pressure broadening work on  $H_2S$  is very limited, and it is more so on its temperature dependence.

During this reporting period, pressure broadening parameters of two pure rotational transitions  $(1_{1,0}$  -  $1_{0,1}$  and  $2_{2,0}$  -  $2_{1,1}$ ) of  $H_2S$  were studied. The broadening gases of  $N_2$ ,  $O_2$ , He, and  $H_2$  were chosen for atmospheric relevance, theoretical interest, and consistency with previous pressure broadening measurements of other molecules reported earlier. The measurements cover a temperature range from 100 K to 600 K.

Pressure broadening cross sections vs temperature for the transition 1(0,1) - 1(1,0) at 168 GHz due to all four broadening gases are shown in Fig. 1. Similar graphs for the transition 2(2,0) - 2(1,1) at 217 GHz are shown in Fig. 2. Plots show that broadening cross sections obey simple power law except the  $H_2S$  - He cross sections which deviate from the power-law. Such deviations are not unexpected when the problem is viewed in the simple qualitative picture of Anderson theory. From the analysis of this theory, we can expect that at some critical temperature, the pressure broadening cross section will exhibit a "roll off" as the temperature decreases. However, there is that velocity considerations from which we expect deviation at lower temperatures for the lighter molecules, but that we also cannot ignore the effects of internal rotational energies. The two effects compete against each other to make it very difficult to predict a deviation from the power-law fit. There need accurate theoretical calculations.

A manuscript is attached which describes variable temperature pressure broadening of  $H_2S$  by  $O_2$  and  $N_2$  (Publication 2)..

#### 3. Pressure Broadening of HNO<sub>3</sub> by Applying FASSST System

Nitric acid is a trace constituents in the stratosphere that plays an important role in the nitrogen and ozone cycles. The rotational spectra of several vibrational states, as well as pressure broadening coefficients of ground state transitions have been widely used in the remote sensing of the upper atmosphere. However, there are only few studies of pressure broadening in the mm/submm spectral region that contains a wide enough data to make possible systematic comparisons with the results of theoretical calculations

a) FASSST System: Figure 3 shows a block diagram of the FASSST system [2]. In the current system, an ISTOK OB-30 is a primary source of millimeter/submillimeter (mm/smm) radiation and is used to cover the 240-375 GHz region. Similar tubes are available from ISTOK for the 100 - 1000 GHz region. The first wire grid polarizer (WG1) provides a well defined polarization from the output of the overmoded BWO waveguide. The second polarizer (WG2) is used to split the output power of the BWO, with ~ 90% being directed quasi-optically through the molecular absorption cell and detected by an InSb hot electron bolometer operating at 1.5 K. The remaining ~ 10% of the power is coupled into a Fabry-Perot (FP) cavity via a mylar beamsplitter (BS1), which provides fringes for frequency interpolation between reference spectral lines of known frequency. In order to provide a highly accurate basis for the analysis of the frequency-voltage characteristic of the BWO, a folded FP cavity FP cavity of length ~ 38.89 m is used to provide modes at every ~3.854 MHz. Provision for a second molecular absorption cell which can be used for calibration purposes is also provided. With this system it is possible to measure thousands of spectral lines per second, with a frequency accuracy of a small fraction of a Doppler width (~-0.1 MHz/3x10<sup>-6</sup> cm<sup>-1</sup>).

Because a single scan contains  $\sim 10^6$  resolution elements, it is not possible to graphically display a complete, full band spectrum. However, Figs. 4-6 show a series of blow ups in both frequency and sensitivity of the mm/smm spectrum of nitric acid (HNO<sub>3</sub>).

b) Results: FASSST system has been applied for the measurements of pressure broadening coefficients of HNO<sub>3</sub>. The speed and versatile of the spectrometer allows the measurement of broadening parameters for a large number of lines. This technique shows its capability to study higher vibrational states, such as,  $v_7 = 1$  vibrational state which is the second lowest lying vibrational state in HNO<sub>3</sub>. Over 7 GHz region, the pressure broadening was fit for 36 transitions, and the results are given in Table 1. Some of these room temperature nitrogen broadened preliminary results are compared to measurements of other investigators and shown in Table 2 The agreement appears to be good. While stronger transmissions agree with previously reported measurements, the weaker transitions should be measured with an improved signal to noise ratio. Work is in progress in this direction.

This technique shows its potential for the first time direct mm and submm measurements of a wide range of quantum states and provide a scope for a systematic comparison with the results of earlier theoretical calculations based on Anderson theory.

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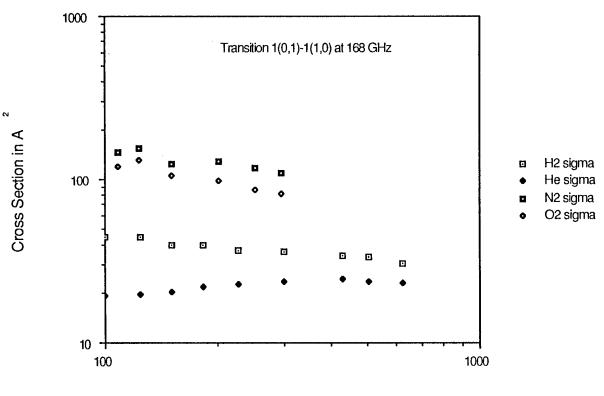
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#### Suggested Topics for Future

- 1) H<sub>2</sub>S and SO<sub>2</sub> self-broadening as a function of a wide range of temperature (80 -600 K) would be useful for theoretical calculations and for remote sensing applications.
- 2) Expanding the pressure broadening of  $H_2S$  due to He to other noble gases, such as A, Ne, and Xe would be interesting to investigate if we still see the deviation from the power law fit that we observe in the  $H_2S$  He system. This investigation would have more theoretical implications and help to identify proper interaction potential.
- 3) Backward wave oscillator based FASSST system has shown its potential for pressure broadening measurements on a large number of lines in ground, as well as excited vibrational state with microwave accuracy. This technique can easily be extended to other molecules of atmospheric importance

(A detailed discussion on this topic is enclosed)

# **Pressure Broadening Cross Section Vs. Temperature of H2S**



Temperature in K

Figure 1.

# Data Sigma Vs. Temperature

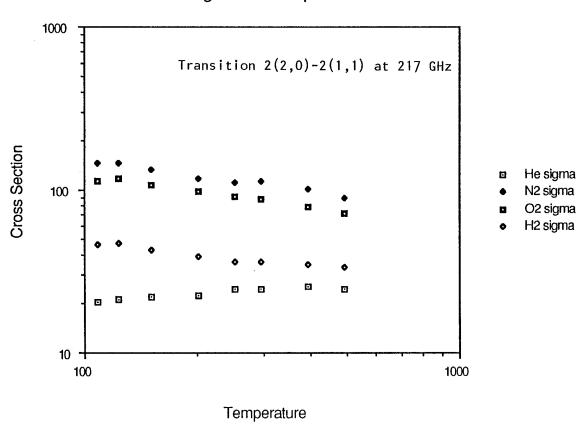
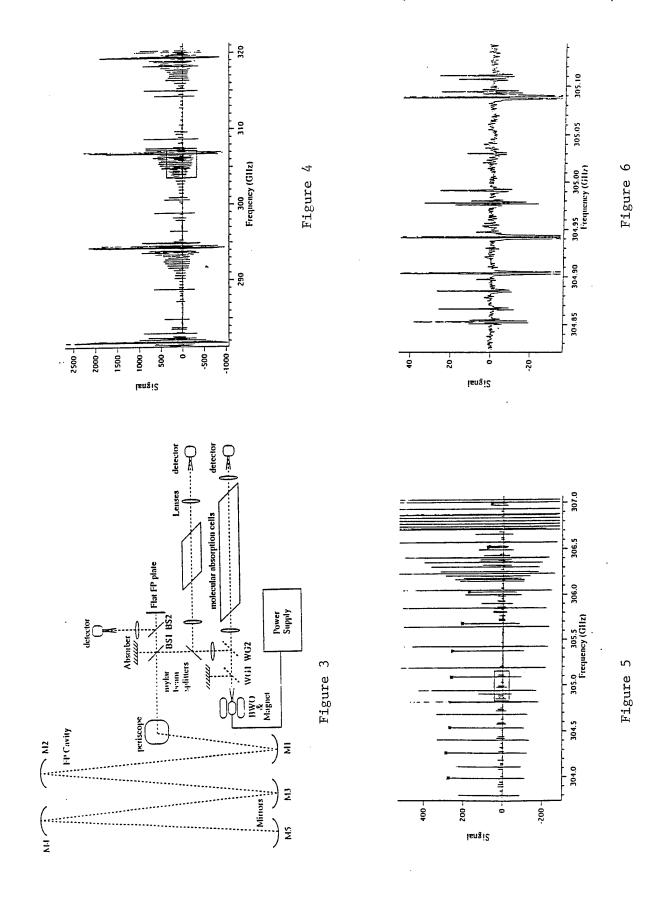


Figure 2.



#### Suggested Topics for Possible Future Consideration

Some of the topics suggested below are aimed at conducting millimeter and submillimeter spectroscopy of molecular species of atmospheric interest applying the newly developed Fast Scan Submillimeter Spectroscopic Technique (FASSST). (1) This technique uses voltage tunable backward wave oscillator (BWO) as a primary source of radiation and uses fast scan ( $\sim 10^5$  Doppler limited resolution elements/s) with a frequency accuracy of a small fraction of a Doppler width ( $\sim 0.1 \ MHz/3x10^{-6} \ cm^{-1}$ ). It has proven to produce high quality pressure broadening data with accuracy similar to the conventional phase-locked klystron-based spectrometer that we used on previous occasions, but with a capability of providing data for thousands of lines in a short time, in comparison to few lines using the conventional broadband spectrometer.

#### The target audience and their subject matter focus

The audience for this work includes both the molecular spectroscopic community and the field measurement community which several federal agencies including AFOSR support, with numerous groups not only at the AF Geophysics Lab at Hanscomb AFB, but at various NASA and NSF supported labs.

#### The goals of the project

The proposed work supports both the scientific and technological goals AFOSR. These include:

- a) Millimeter and Submillimeter Spectroscopy: AFOSR has extensive personnel and facilities in areas central to AFOSR's mission whose work is based upon the spectroscopic data base. The major scientific goal of this project is to contribute to the atmospheric and astrophysics data base.
- b) Education of Students and Introduction into the AFOSR System: As in earlier NCCU projects students will be significantly involved. This will not only help undergraduates to prepare for successful graduate careers, but also make both graduates and undergraduates aware of the excitement of AFOSR opportunities.

#### The means to accomplish the goal.

a) This laboratory has successfully undertaken a number of projects in the millimeter and submillimeter region over the last 15 years. These have been funded by a number of agencies including NASA, DoE, AFOSR, and ARO. This work has resulted in publications on the development of relativistic e-beam mm/smm sources, <sup>(2,3)</sup> diagnostic measurements of bunched relativistic electron beams, <sup>(4)</sup> pressure broadening in the mm/smm spectral region, <sup>(5-9)</sup> and the measurement of the millimeter wave dielectric properties of gyrotron window materials. <sup>(10-12)</sup>

Most recently, NCCU has become involved with the development of a new Fast Scan Submillimeter Spectroscopic Technique (FASSST) and its application in collaboration with the Ohio State University. A mirror site for the analysis of spectral data has been established at NCCU. This system will play an important role in the execution of the tasks proposed below.

#### b) Specific Spectroscopic Projects:

In general the important atmospheric, planetary, and interstellar species are relatively small molecules. In many cases the same species (e. g. water) is important in all three environments. In general both the positions of lines and their broadening parameters are important. For the earth the most important broadening species are nitrogen and oxygen, for a planet like Venus or Mars carbon dioxide, and for the outer planets hydrogen and helium. The following are examples of important projects:

- 1) Line positions and broadening parameters for HNO<sub>3</sub> and its vibrational states.
- 2) Expand the pressure broadening measurements on H<sub>2</sub>S and SO<sub>2</sub>.

Nitric acid is a trace constituent in the stratosphere that plays an important role in the nitrogen and ozone cycles. Accurate knowledge of line positions at various vibrational states and pressure broadening coefficients is important in the remote sensing of the upper atmosphere. Because each vibrational state is essentially a separate spectroscopy project of significance, the analyses of even few of these states would be a significant accomplishment. Thus, it is important to have a realistic understanding of the scope of the project and its expected results in the context of available time and resources. Some preliminary results of the rotational transitions of nitric acid in the  $v_7 = 1$  vibrational states as well as pressure broadening measurements of nitric acid are included in the attached final report. The  $v_7 = 1$  has a vibrational energy of 580 cm<sup>-1</sup> and is the second lowest lying vibrational state in nitric acid.

We also propose to perform additional pressure broadening measurements on H<sub>2</sub>S and SO<sub>2</sub>. The proposed high resolution measurements will be performed using the newly developed fast scan technique (FASSST) which will provide a scope to analyze a large number of lines and make possible a systematic comparison with the results of earlier theoretical calculations based on Anderson theory. Temperature dependent self-broadening data will be useful for theoretical calculations and remote sensing applications. (13) Expanding the pressure broadening results due to He to other broadening gases, such as, A, Ne, and Xe would be interesting to investigate if we still see the deviation that we observed in the H<sub>2</sub>S -He system. (14) Emphasis will be on the measurement of pressure broadening parameters and their temperature dependence. The past several years have seen an increase in the experimental and theoretical investigations of pressure broadening parameters of atmospherically relevant molecules. Unfortunately, the temperature dependence of pressure broadening remains relatively unexplored. Accurate characterization of the temperature variation of broadening parameters over the range of atmospheric temperatures is necessary for a proper analysis of spectra obtained from remote sensing instruments and developing theoretical model for the upper atmosphere chemistry.

#### c) The Experiment:

A brief description of the new spectroscopic system and some examples of the recorded spectra are included in the attached final report. This brief discussion demonstrates the method and feasibility of the proposed work. The capabilities of this system to acquire large amounts of complex mm/smm spectra rapidly are the most likely aspects of this project to produce change.

d) Dissemination Plan and plans to evaluate the project: In order for this project to meet its final goal the data and scientific work must be available to the end users. The proposed research is designed to contribute data to the HITRAN high-resolution molecular database, maintained by the AF Philips Laboratory. Additionally, as will all good scientific work the result will be published and fully described in the open literature.

For this project success should also be measured in terms of human resources. Graduates and undergraduates involved in the previous research had the opportunities to present their research results to various national meetings. We expect similar, measurable success as a result of this program.

#### Budget comment:

Over the past 10 years to enhance the mm/smm spectroscopy research capability, NCCU had received several instrumentation grants/contracts from a variety of agencies including AFOSR. As a result most of the measurement systems needed to pursue this research are in place and funds are sought at least at the current level for operating expenses and salaries.

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- [13] Dr. Linda Brown of JPL commented on the need for such data during the presentation of our work on H<sub>2</sub>S at the International Symposium on Molecular Spectroscopy, Columbus, OH, June 1996.

[14] Dr. Gamache from U. Mass-Lowell Center for Atmospheric Research, commented about the importance of having accurate temperature dependent pressure broadening data for molecular force calculation. To understand the low temperature behavior of H<sub>2</sub>S-He system, he remarked about the importance of having additional data using other noble gases as collision partners. International Symposium on Molecular Spectroscopy, Columbus, OH, June 1996.

# VARIABLE TEMPERATURE PRESSURE BROADENING OF H<sub>2</sub> S BY O<sub>2</sub> AND N<sub>2</sub>

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Abstract-Pressure broadening parameters of two ground vibrational state rotational transitions of  $H_2S$  have been measured for the broadening gases  $N_2$  and  $O_2$ . Temperatures range from 100 to 600 Kelvin, and the broadening parameters obey a standard power-law temperature dependence over the whole range. This temperature dependence is compared with results of similar studies involving other molecules. Room temperature broadening parameters are compared with experimental results from infrared studies.

# INTRODUCTION

The past several years have seen an increase in the experimental and theoretical investigations of pressure broadening parameters of atmospherically relevant molecules. Unfortunately, the temperature dependence of pressure broadening remains relatively unexplored. Accurate characterization of the temperature variation of broadening parameters over the range of atmospheric temperatures is necessary for a proper analysis of spectra obtained from remote sensing instruments. Experimentally determined broadening parameters also help verify theoretical calculations or promote interest in new theoretical studies.

Hydrogen sulfide (H<sub>2</sub>S) is typically introduced into the earth's atmosphere by volcanoes or by oil and gas refineries. Pressure broadening data for H<sub>2</sub>S is sparse, and we have been unable to find any theory calculations in the literature. The most complete room temperature data come from infrared experiments.<sup>1-5</sup> Previous to the present work, the only available temperature dependent data was for broadening with H2 and He.<sup>6</sup>

We present here foreign gas pressure broadening parameters of  $H_2S$  with  $O_2$  and  $N_2$  over a temperature range from 100 to 600 K. We have measured broadening parameters for two ground vibrational state rotational transitions:  $I_{1.0}$ - $I_{0.1}$  (centered at 168762.762 MHz) and  $I_{2.0}$ - $I_{1.1}$  (centered at 216710.435 MHz). The room temperature values are compared to the measured air broadening parameters of Waschull et al<sup>2</sup> and Sumpf et al.<sup>3</sup> The temperature dependence parameters are compared to previous measurements involving the  $I_{1.0}$ - $I_{1.0}$ 

#### EXPERIMENTAL DETAILS

The millimeter wave system employed in this experiment has been described in detail elsewhere. <sup>13,14</sup> Briefly, the output of a phase-locked 10-15 GHz YIG oscillator is tripled and subsequently amplified by a 1-Watt, 26-40 GHz Traveling Wave Tube amplifier. The amplifier output is frequency multiplied by a crossed waveguide harmonic generator, and the millimeter wave radiation is propagated quasi-optically through the absorption cell. A liquid helium cooled InSb hot electron bolometer measures changes in the source power as it is absorbed by the H<sub>2</sub>S gas.

The millimeter waves were swept rapidly in frequency through the absorption line, allowing us to record true lineshapes, since the detection system had sufficient bandwidth to preserve all Fourier components of the lineshape. A least-squares fit of the lineshape to a Voigt profile allowed us to extract the Lorentzian halfwidth. Baseline undulations (reflections within the optical path) were also preserved by the detection bandwidth, complicating fits of the lineshapes to the Voigt profile. Baseline effects were minimized by adjusting the millimeter wave optics, and whatever baseline remained was fit to a quadratic function of frequency. Figure 1 shows an example of a recorded lineshape atop a slightly curved baseline.

#### \*\*\*\*\* INSERT FIG. 1 HERE \*\*\*\*\*

A 2-foot long quartz equilibrium cell was used for all of the measurements. Surrounding the cell was a 4-foot long copper jacket, which was heated electrically or cooled by liquid nitrogen. Temperatures between 100 and 600 Kelvin could easily be maintained. The additional length of the copper jacket was to ensure the ends of the quartz cell are at the same temperature as the center. Chromel-alumel thermocouples located at the center and ends of the cell were used to record the cell temperature. For temperatures

below 300 K, a feedback mechanism involving an Omega CN2001 Programmable

Temperature Controller and a computer controlled valve regulated the flow of liquid

nitrogen through tubes soldered to the copper jacket. Above room temperature, variable

voltages were applied to resistive heating braids wrapped around the length of the copper

jacket.

Gas pressure inside the cell were measured by an MKS Baratron capacitance manometer. The cell would be filled  $H_2S$  at pressures less than 1 mTorr (to avoid self broadening), and then the  $O_2$  and  $N_2$  gases were added through a computer controlled valve. Roughly 40 lineshapes were recorded over a pressure range up to 0.5 Torr. Figure 2 shows an example of the dependence of the fitted Lorentzian halfwidth on foreign gas pressure. Employing the method of Takaishi and Sensui, 15 we estimate that thermal transpiration effects were less than 3%, and that broadening parameters were altered by less than 1%.

\*\*\*\*\* INSERT FIG. 2 HERE \*\*\*\*\*

#### RESULTS AND DISCUSSION

The O<sub>2</sub> and N<sub>2</sub> broadening parameters of H<sub>2</sub>S for each of the two transitions studied are given in Tables 1 and 2.<sup>†</sup> Figures 3 and 4 show the broadening parameters plotted vs temperature on a logarithmic scale. Systematic errors are estimated at 5% for these measurements, as discussed in Ref. 9. For the entire temperature range, the data obey a simple power-law temperature dependence:

$$\gamma(T) = \gamma \left(T_0 \left(T_0 / T\right)^n\right) \tag{1}$$

where  $\gamma(T_0)$  is the pressure broadening parameter at the reference temperature  $T_0$ =300 K and n is a constant exponent of the temperature. Table 3 lists the fitted values of  $\gamma(T_0)$  and n for each broadening gas and each transition. Figures 3 and 4 also show the fitted power-law curves to the data. Within the error, these values show no observable state dependence for the two transitions studied.

\*\*\*\*\* INSERT TABLES 1, 2, AND 3 HERE \*\*\*\*\*

\*\*\*\*\* INSERT FIGS. 3 AND 4 HERE \*\*\*\*\*

In previous work by this research group, SO<sub>2</sub><sup>7</sup> and HNO<sub>3</sub><sup>8.9</sup> broadening parameters were shown to obey Equation 1 over the entire range of temperatures in those studies. H<sub>2</sub>O<sup>10.11</sup> and HDO,<sup>12</sup> however, do not. Below 150 K, these broadening parameters deviate from the power-law prediction, becoming smaller than expected. This behavior is understood in the context of the theory of Anderson, as modified by Tsao and Curnutte. As the collision energy is reduced, Fourier components generated by the collision are reduced and become insufficient for significant broadening.<sup>10,12</sup> Presumably, for the 100 to 600 K range of temperatures, H<sub>2</sub>S energy levels are sufficiently dense that broadening

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<sup>&</sup>lt;sup>†</sup> Note that no broadening parameters are reported for  $O_2$  broadening above 520 K. At these temperatures, the lineshapes would disappear, presumably due to the oxidation of  $H_2S$ . This phenomenon was not observed in the case of  $N_2$  broadening, nor in the He and  $H_2$  broadening of Ref. 6.

efficiency is not reduced. We can speculate that below 100 K, we would expect to see a similar deviation from Equation 1 as in the cases of H<sub>2</sub>O and HDO. Such an experiment is possible with the collisional cooling technique, but in practice would be prohibitively difficult, as there is a range of about 10-20 K between the lowest temperature which yields equilibrium data, and the highest temperature which yields collisional cooling data. We do, however, observe such a deviation in the case of helium gas broadening.<sup>6</sup>

Currently, there are no other published works, to our knowledge, with which we can compare our temperature dependent measurements. We have also been unable to find any theory calculations for  $H_2S$  broadening with  $N_2$  or  $O_2$ . We can, however, compare the room temperature values of our results to air broadening measurements in the infrared by Waschull et al and by Sumpf et al.<sup>2,4</sup> Figure 5 shows the room temperature broadening parameters in the  $v_1$ ,  $v_2$ , and  $v_3$  vibrational states, as well as our ground vibrational state measurements. We have calculated air broadening coefficients from our  $N_2$  and  $O_2$  data by the equation:

$$\gamma(\text{air}) = 0.8 \, \gamma(N_2) + 0.2 \, \gamma(O_2)$$
 (2)

Though we only measured two transitions, it is clear that these measurements are consistent with each other.

\*\*\*\*\* INSERT FIG. 5 HERE \*\*\*\*\*

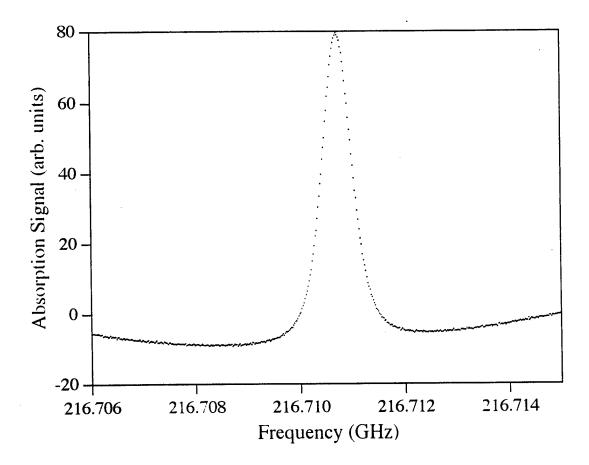
#### **SUMMARY**

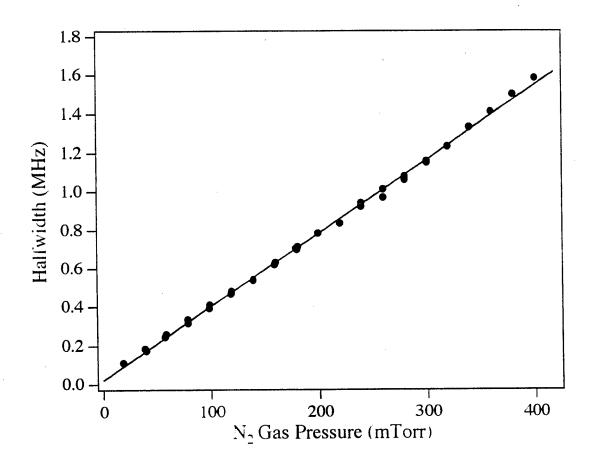
We have presented the first measurements of the temperature dependence of the pressure broadening of  $H_2S$  by  $N_2$  and  $O_2$ . These accurate millimeter wave measurements show that the broadening parameters obey a power-law temperature dependence over the 100 to 600 K temperature range. These results are consistent with similar measurements of  $SO_2$  and  $HNO_3$ , in that the broadening parameters do not deviate from the power-law, like  $H_2O$  and HDO in the same temperature range. Theoretical calculations are currently tacking and are needed to verify these measurements. However, the room temperature values for the  $H_2S$  broadening are consistent with previous studies in the infrared regime.

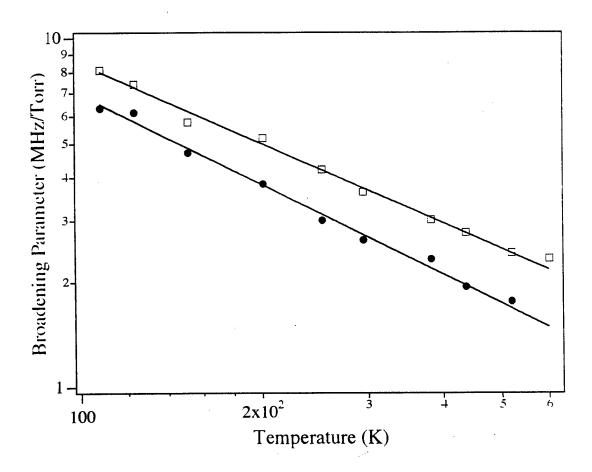
Acknowledgments—We would like to thank NASA for the support of this work and the Air Force Office of Scientific Research for its support of J.D.'s work. This work was also made possible by the Max Planck Research Prize awarded to F.C.D, and a NASA Global Change Fellowship awarded to C.D.B.

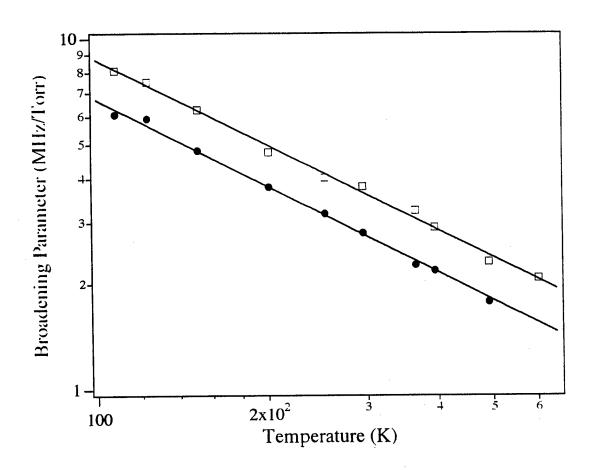
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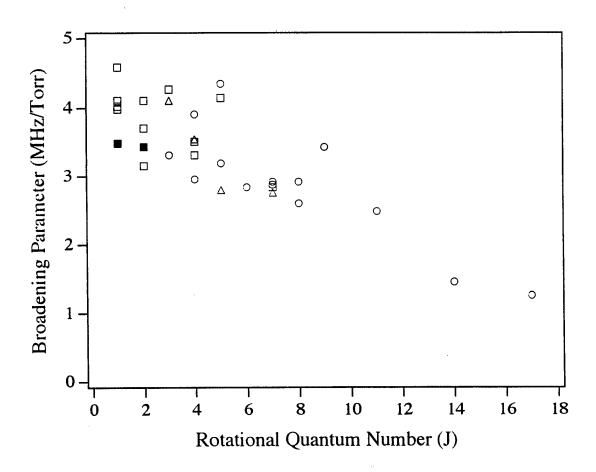
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## FIGURE CAPTIONS

- Fig. 1. Example of the lineshape data and curved baseline.
- Fig. 2. Example plot of Lorentzian halfwidth vs broadening gas pressure ( $N_2$  at 295 K for this case).
- Fig. 3. Measured  $N_2$  (open squares) and  $O_2$  (solid circles) pressure broadening parameters of the  $1_{1.0}$ - $1_{0.1}$  transition of  $H_2S$  (logarithmic scale). Solid lines are the result of a least-squares fit to Eq. (1).
- Fig. 4. Measured  $N_2$  (open squares) and  $O_2$  (solid circles) pressure broadening parameters of the  $2_{2,0}$ - $2_{1,1}$  transition of  $H_2S$  (logarithmic scale). Solid lines are the result of a least-squares fit to Eq. (1).
- Fig. 5. Comparison of room temperature air broadening parameters as a function of J''. Data includes the ground vibrational state (solid squares) of this work,  $v_2$  (open squares) of Ref. 2, and  $v_1$  (open circles) and  $v_3$  (open triangles) of Ref. 4.

Temperature (K)	$\gamma(N_2)$ (MHz/Torr)	γ(O <sub>2</sub> ) (MHz/Torr)
108	8.10	6.08
123	7.53	5.91
151	6.27 4.76	4.81 3.79
201 252	4.76	3.19
295	3.80	2.81
365	3.25	2.27
395	2.91	2.19
492	2.32	1.78
602	2.08	

Temperature (K)	$\gamma(N_2)$ (MHz/Torr)	$\gamma(O_2)$ (MHz/Torr)
108	8.11	6.32
123	7.40	6.16
151	5.77	4.71
201	5.20	3.83
2 <i>5</i> 2	4.22	3.01
295	3.64	2.64
382	3.02	2.33
436	2.78	1.94
520	2.43	1.76
602	2.34	

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*y*.

	$1_{1.1} - 1_{0.1}$		2 <sub>2.0</sub> - 2 <sub>1.1</sub>	
	N <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>	$O_2$
γ(300 K)	3.69(7)	2.70(7)	3.61(5)	2.74(5)
n	0.76(3)	0.86(4)	0.80(2)	0.81(3)

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# **TABLE CAPTIONS**

- Table 1. Measured  $N_2$  and  $O_2$  broadening parameters at various temperatures for the  $1_{1,0}$ .  $1_{0,1}$  transition of  $H_2S$ . Absolute uncertainty is estimated at  $\pm 5\%$ .
- Table 2. Measured  $N_2$  and  $O_2$  broadening parameters at various temperatures for  $2_{2.0}$ - $2_1$  transition of  $H_2S$ . Absolute uncertainty is estimated at  $\pm 5\%$ .
- Table 3. Least-squares fit results for g(T0) and n for both transitions and both broadening gases. Uncertainties are one standard deviation taken from the fit.